Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

The New Triazine-based Porous Copper Phosphonate $[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$

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Table S1 List of crystalline porous metal phosphonates, whose porosity was proven by gas sorption measurements.

Formula sum	Phosphonic acid	Literature
β-$Al_2(CH_3PO_3)_3$	Methylphosphonic acid	1
α-$Al_2(CH_3PO_3)_3$	Methylphosphonic acid	2
$[M_2(H_2O)_2(L1)]\cdot xH_2O$; M= Mg, Mn, Fe, Co, Ni	H_4L1=N,N‘-piperazinebis (methylenephosphonate)	3
$[Ti(O)(H_2L1)]\cdot nH_2O$ $[Al(OH)(H_2L1)]\cdot nH_2O$	H_4L1 = N,N‘-piperazinebis(methylenephosphonate)	4
$[Ln((H_2L2)_3]\cdot 2H_2O$; Ln= Tb, Dy, Eu, Gd	H_3L2= N-(phosphonomethyl) proline	5
$[Cu_3(H_3L3)(OH)(H_2O)_3]\cdot H_2O\cdot CH_3OH$	H_8L3= 1,3,5,7-tetrakis(4-phenylphosphonic acid)-adamantane	6
$Sr_2(H_2L4)(CH_3OH)(H_2O)_4$	H_6L4=1,3,5-tris(4-phosphonophenyl)benzene	7
$M_2(H_2L)_3\cdot 7H_2O$; M= Gd-Yb, Y, Sc	H_4L5= N,N′-2-methylpiperazinebis(methylene phosphonic acid)	8
$Cu(C_2H_4N_4)$ $(H_2L6)H_2O$	$C_2H_4N_4$= Aminotriazole, H_4L6= 1,4-dihydrogenphosphonate	9
$[M_2(H_2O)_2L7]\cdot 11H_2O$; M= Ni, Co	H_4L7= N, N'-4,4'-bipiperidinebis-(methylenephosphonic acid)	10
$Zr_3(H_3L8)_4\cdot 15H_2O$	H_6L8= 1,3,5-Tris(4-phosphonophenyl)benzene	11
$Al(H_3L9)(H_2O)$	H_6L9= (2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene) triphosphonic acid	12

Table S2 Investigated ratios and amount of chemicals used for the crystallization diagram (Fig. 2). $Cu(NO_3)_2$ and NaOH were used as 2M aqueous solution.

Molar ratio			Amount of chemicals				Product
H_6PPT	$Cu(NO_3)_2$	NaOH	H_6PPT[mg]	H_2O[µL]	Cu^{2+}[µL]	NaOH[µL]	
1	1	1	20.0	164	18	18	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	1	1.5	20.0	154	18	27	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	1	2	20.0	145	18	36	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	1	3	20.0	127	18	54	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	1	4	20.0	109	18	73	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$+ not identified product
1	1	6	20.0	73	18	109	$Cu_2NO_3(OH)_3$
1	2	0.25	20.0	159	36	5	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	2	0.5	20.0	154	36	9	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	2	1	20.0	145	36	18	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	2	1.5	20.0	136	36	27	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	2	2	20.0	127	36	36	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	2	3	20.0	109	36	55	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$+ not identified product
1	2	4	20.0	91	36	73	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$+ not identified product
1	2	6	20.0	54	36	109	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$+ not identified product
1	3	0.5	20.0	136	54	9	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	3	1	20.0	127	54	18	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	3	2	20.0	109	54	36	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$+ not identified product
1	3	3	20.0	91	54	55	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$+ not identified product
1	3	4	20.0	73	54	73	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$+ not identified product
1	1.5	0.5	20.0	164	27	9.	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	1.5	1	20.0	154	27	18	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	1.5	1.5	20.0	145	27	27	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	2	0	20.0	164	36	0	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	5	0	20.0	109	91	0	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$
1	5	1	20.0	91	91	18	$[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$+ not identified product
1	5	2	20.0	73	91	36	not identified product
1	5	3	20.0	54	91	55	not identified product
1	5	4	20.0	36	91	73	$Cu_2NO_3OH_3$
1	5	5	20.0	18	91	91	$Cu_2NO_3OH_3$
1	0.5	0.25	20.0	186	9	5	X-ray amorphous
1	0.5	0.5	20.0	182	9	9	X-ray amorphous
1	0.5	1	20.0	173	9	18	X-ray amorphous
1	0.5	1.5	20.0	164	9	27	X-ray amorphous
1	0.33	0.17	20.0	191	6	3	X-ray amorphous
1	0.33	0.33	20.0	188	6	6	X-ray amorphous
1	0.33	0.67	20.0	182	6	12	X-ray amorphous
1	0.33	1	20.0	176	6	18	X-ray amorphous
1	0.67	0.33	20.0	182	12	6	X-ray amorphous
1	0.67	0.67	20.0	176	12	12	X-ray amorphous
1	0.67	1	20.0	170	12	18	X-ray amorphous
1	0.17	0.17	20.0	194	3	3	X-ray amorphous
1	0.17	0.33	20.0	191	3	6	X-ray amorphous

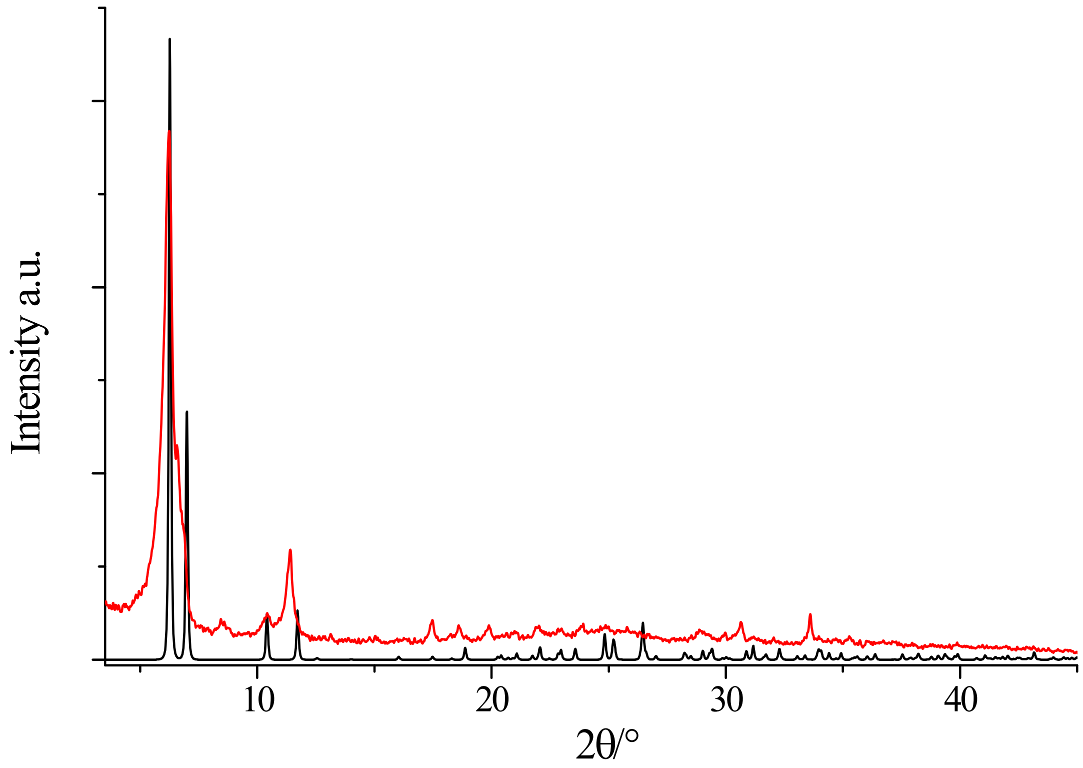

Fig. S1 Not identified product (red line) and calculated powder pattern for $[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$ (black line).

Table S3 Crystallographic parameters of $[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$.

Formula sum	$C_{21}H_{12}Cu_3N_3O_{15}P_3$
Formula weigh / gmol^{-1}	829.87
Temperature / K	120
Wavelength	0.68890
Crystal system	Monoclinic
Space group	*Cm*
a/ Å	25.618(5)
b/ Å	17.040(3)
c/ Å	4.4322(9)
β/ °	99.96(3)
Volume/ Å^3	1905.6(7)
Z	2
Density (calculated) / gcm^{-3}	1.446
Adsorption coefficient	1.630
F(000)	822
θ min-max / °	2.80, 24.52
limiting indices: h, k, l	-30 / 30, -20 / 20, -5 / 5
Reflections collected/ unique	7534/ 2946
R_{int}	0.0596
Observed data [I>2σ(I)]	2773
Number of reflections, parameters, restraints	2946, 228, 2
Solution method	Direct methods ShelXS
Refinement method	Least-squares ShelXL
GOF	1.091
R1 (all data)	0.0532
R1 (I>2sigma(I))	0.0500
wR2 (all data)	0.1521
wR2 (I>2sigma(I))	0.1436
Residual electron density / eÅ^{-3}	min.-0.630, max. 0.625
Flack parameter	0.66(4) refined as inversion twin

Table S4 Selected bond lengths of $[Cu_3(PPT)(H_2O)_3]\cdot10H_2O$.

Atom 1	Atom 2	Bond lengths [Å]	Atom 1	Atom 2	Bond lengths [Å]
Cu1	O5	1.956(7)	C1	C2	1.365(14)
Cu1	O4	1.972(6)	C1	C6	1.408(16)
Cu1	O1	2.320(13)	C2	C3	1.409(14)
Cu2	O7	1.915(6)	C3	C4	1.393(16)
Cu2	O3	1.936(6)	C4	C5	1.370(14)
Cu2	O2A	2.030(14)	C4	C7	1.517(12)
Cu2	O2B	2.06(2)	C5	C6	1.412(15)
Cu2	O6	2.123(5)	C7	N2	1.335(12)
Cu2	O4	2.147(7)	C7	N1	1.328(11)
P1	O5	1.523(7)	N2	C8	1.355(9)
P1	O3	1.523(8)	C8	C9	1.492(18)
P1	O4	1.549(6)	C9	C10	1.364(11)
P1	C1	1.807(9)	C10	C11	1.387(14)
P2	O7	1.513(6)	C11	C12	1.386(12)
P2	O6	1.536(9)	O9	N1	2.962(36)
P2	C12	1.840(13)	O8	O9	2.757(28)
			O2A	O8	2.823(26)
			O2B	O8	2.758(28)

Table S5 Selected angles of $[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$.

Atom 1	Atom 2	Atom 3	Angle [deg]	Atom 1	Atom 2	Atom 3	Angle [deg]
O5	Cu1	O5	90.6(4)	C2	C1	C6	118.2(9)
O5	Cu1	O4	89.3(3)	C2	C1	P1	120.6(8)
O5	Cu1	O4	168.8(3)	C6	C1	P1	121.2(7)
O4	Cu1	O4	88.5(4)	C1	C2	C3	121.6(10)
O5	Cu1	O1	93.0(3)	C4	C3	C2	119.3(9)
O4	Cu1	O1	98.2(3)	C5	C4	C3	120.5(9)
O7	Cu2	O3	171.1(3)	C5	C4	C7	120.3(9)
O7	Cu2	O2A	81.4(5)	C3	C4	C7	119.3(8)
O3	Cu2	O2A	90.2(6)	C4	C5	C6	119.4(10)
O7	Cu2	O6	92.8(3)	C5	C6	C1	120.9(9)
O3	Cu2	O6	94.3(3)	N2	C7	N1	125.4(8)
O2A	Cu2	O6	161.5(8)	N2	C7	C4	117.8(8)
O7	Cu2	O4	96.1(3)	N1	C7	C4	116.8(8)
O3	Cu2	O4	88.1(3)	C7	N1	C7	115.2(11)
O2A	Cu2	O4	99.3(8)	C7	N2	C8	115.4(8)
O6	Cu2	O4	98.8(3)	N2	C8	N2	123.1(11)
Cu1	O4	Cu2	105.8(3)	N2	C8	C9	118.4(6)
O5	P1	O3	114.5(4)	C10	C9	C10	120.4(12)
O5	P1	O4	110.5(4)	C10	C9	C8	119.8(6)
O5	P1	C1	109.5(4)	C9	C10	C11	119.8(9)
O3	P1	O4	110.1(4)	C12	C11	C10	120.8(9)
O3	P1	C1	103.9(4)	C11	C12	C11	117.6(12)
O4	P1	C1	108.0(4)	O7	P2	O7	115.2(5)
P1	O3	Cu2	132.1(4)	O7	P2	O6	110.8(3)
P1	O4	Cu1	133.1(4)	O7	P2	C12	107.7(3)
P1	O4	Cu2	120.8(4)	O6	P2	C12	104.0(5)
P1	O5	Cu1	122.6(4)	P2	O6	Cu2	116.7(3)
P2	O7	Cu2	132.7(4)	Cu2	O6	Cu2	118.9(4)
C11	C12	P2	121.2(6)				

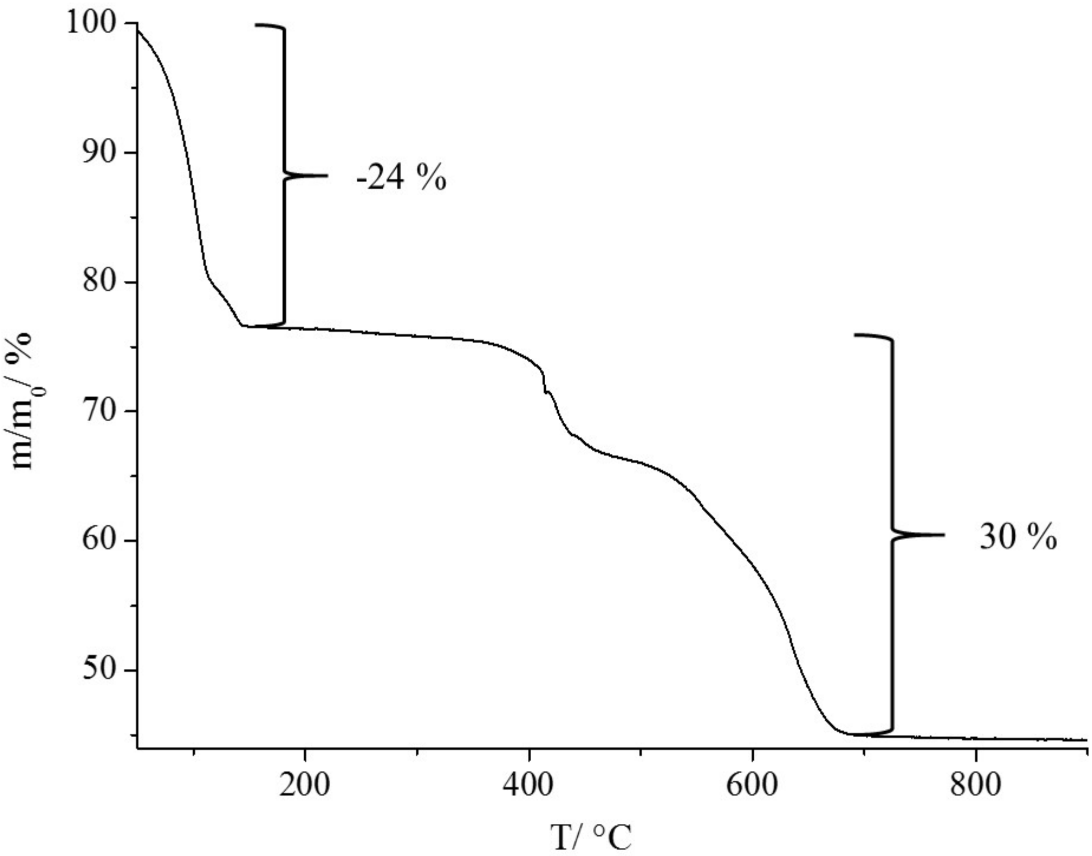

Fig. S2 Results of the thermogravimetric measurement of $[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$.

Table S6 Thermogravimetric measurement of $[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$.

	Temperature	Change of weight	Reaction, calculated weight loss
1. Step	up to 200°C	- 24 %	removal of water molecules (24 %)
2. Step	380° C up to 800 °C	- 30 %	Thermal decomposition of the framework. (29 %)

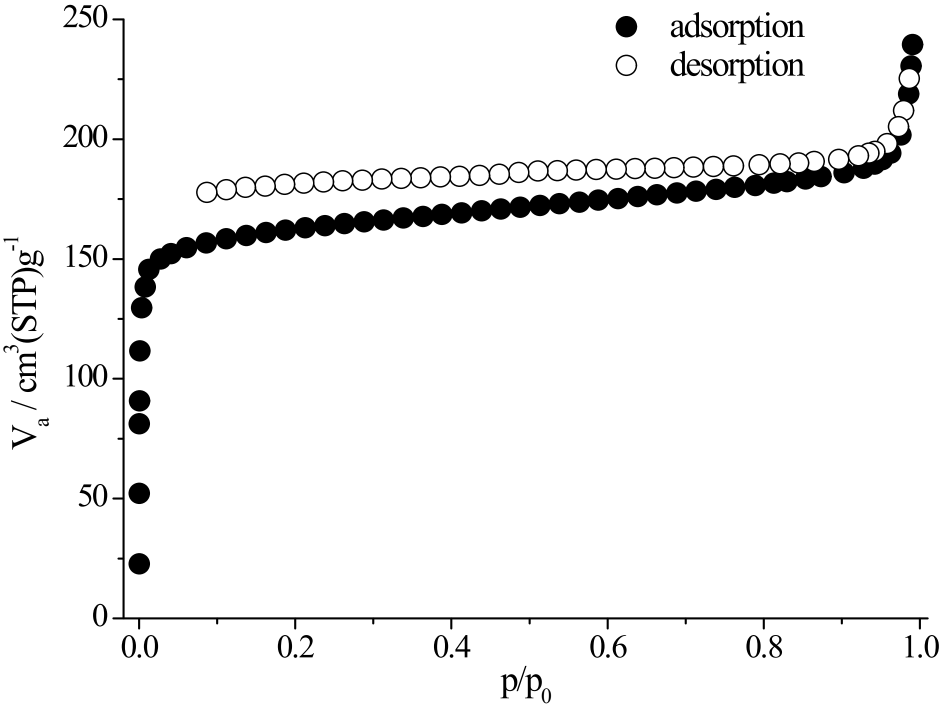

Fig. S3 N_2 sorption measurement recorded at 77 K of $[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$.

Table S7 Repeated N_2 sorption measurements of $[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$.

	V_{mic} [cm³/g]	a_{sBET} [m²/g]
1	0.28	691
2	0.28	726
3	0.29	739

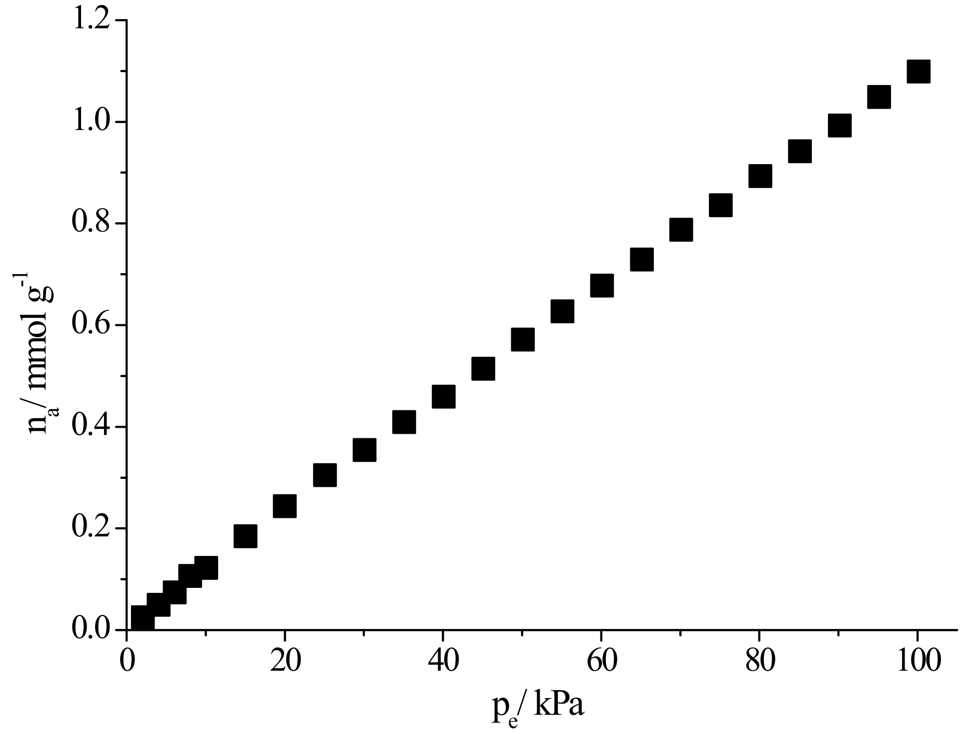

Fig S4 CO_2 sorption measurement recorded at 298.15 K of $[Cu_3(PPT)(H_2O)_3]\cdot10H_2O$.

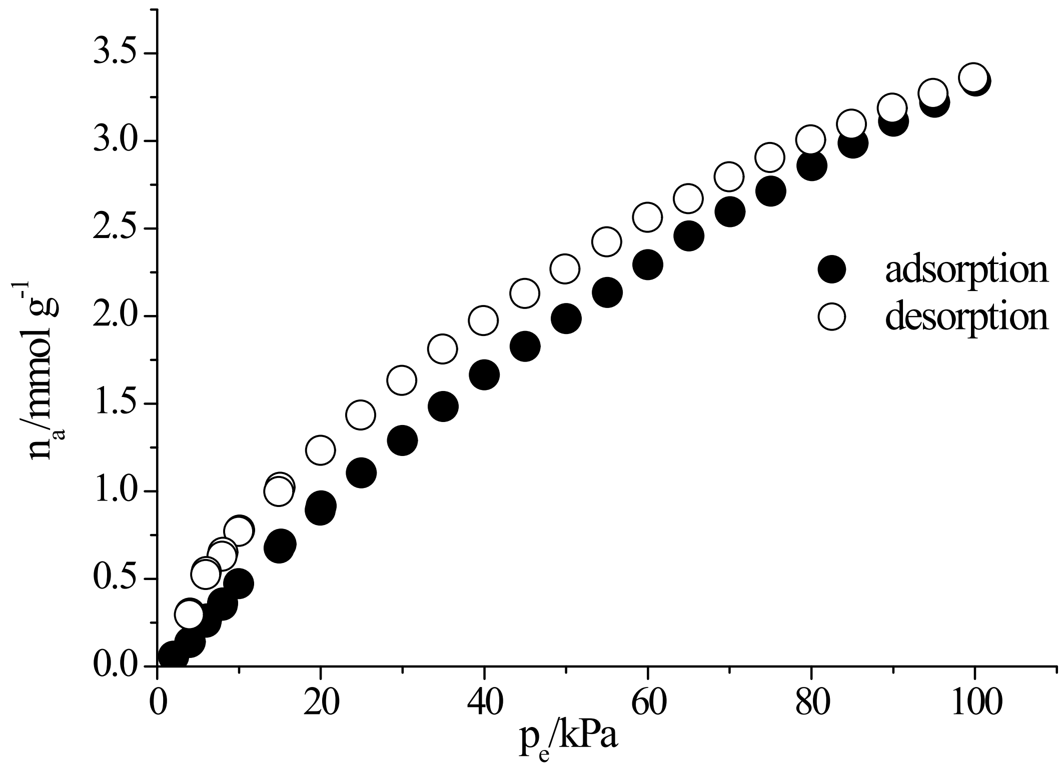

Fig S5 H_2 sorption measurement recorded at 77 K of $[Cu_3(PPT)(H_2O)_3]\cdot10H_2O$.

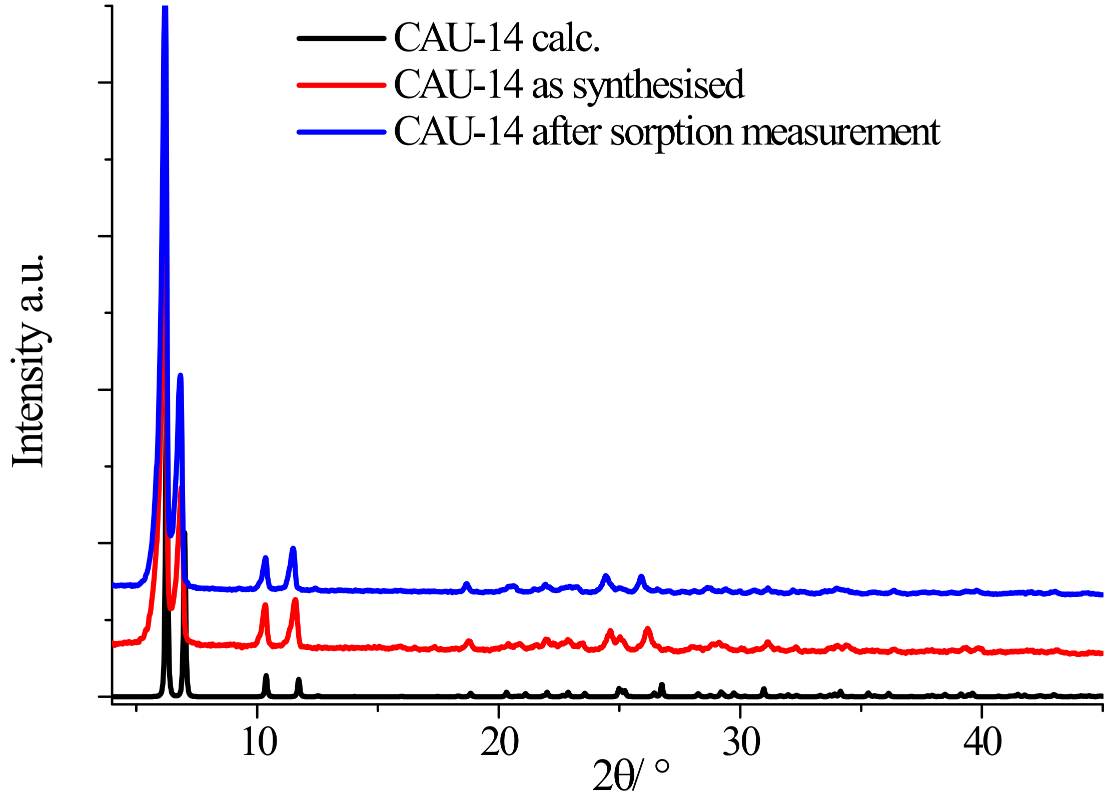

Fig. S6 Comparison of the PXRD patterns of as-synthesized CAU-14 and CAU-14 after the sorption measurements with the simulated PXRD pattern based on the single crystal data.

Experimental

Chemicals

Chemicals were used as received without further purification.

Table S8 Used chemicals.

chemical	producer
Aqueos Ammonia 25%	Wall
4-Bromobenzonitrile, 99%	Aldrich
Bromotrimethylsilane	Aldrich
Chloroform	Wall
$Cu(NO_3)_2 \cdot 3\ H_2O$	Merck
Dichlormethane	Grüssing
Diethyl ether	Roth
1,3-Diisopropylbenzene	Aldrich
Ethanol 99%, 1% MEK	Wall
1,3-*Iso*propylbenzole	Aldrich
$Mg(SO_4)$	Merck
Methanol	BASF
NaCl	Merck
$Na_2CO_3 \cdot 10\ H_2O$	Grüssing
NaOH p.a.	Grüssing
$NiCl_2 \cdot 6\ H_2O$	Merck
Sulfuric acid 96%	BASF
Triethylphosphite	Aldrich
Trifluormethane sulfonic acid, 99%	ABCR

Synthesis of 2,4,6-*tri*-(4-bromophenyl)-*s*-triazine

17.5 mL (29.9 g, 199 mmol) trifluormethane sulfonic acid were slowly added to 10 g (55 mmol) of 4-bromobenzonitrile. It was stirred for 20 h and afterwards 60 mL of deionised water was added. The mixture was neutralised with aqueous ammonia. The colourless solid was filtered under vacuum and washed with deionised water and chloroform. 9.74 g (17.8 mmol, yield 97 %) of colourless solid were recovered.

The solid was not soluble in available solvents for NMR spectroscopy.

Elemental analysis: Calculated for $C_{21}H_{12}N_3Br$: C = 46.1 %, H = 2.2 %, N = 7.7 %, Found: C = 45.8 %, H = 2.2 %, N = 7.8 %.

IR $\tilde{v}$ (cm^{-1}) = 3069 (w, C-H str.), 3043 (w, C-H str.), 1590 (w, C=C str.), 1578 (s, C=C str.), 1541 (m, triazine ring str.), 1509 (s,b, triazine ring str.), 1485 (s, C=C str.), 1400 (m, C=C str.), 1368 (m, C=C str.), 1353 (s,b, triazine ring str.), 1290 (m, C-H), 1277 (w, C-H def.), 1235 (w,b, C-H), 1172 (m, C-H def.), 1066 (m, C-Br), 1008 (s, triazine ring str.), 859 (w, C-H def.), 841 (m, triazine bend.), 802 (s, C-H def.), 704 (C-H def.), 628 (w, arom. ring def.), 494 (s, C-Br str.), 474 (s, arom. ring def.).

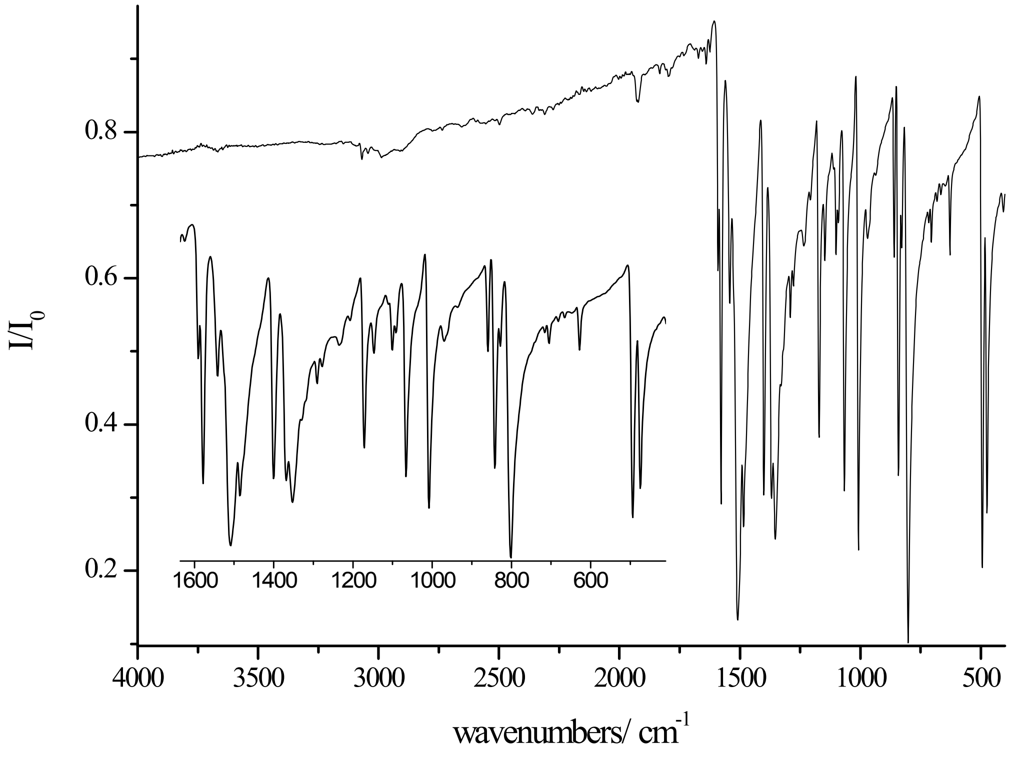

Fig S7 IR spectrum of 2,4,6-*tri*-(4-bromophenyl)-*s*-triazine.

Synthesis of 2,4,6-*tri*-(4-diethylphosphonophenyl)-*s*-triazine

$NiCl_2 \cdot 6H_2O$ was dried at 150 °C.

8.550 g (15.7 mmol) 2,4,6-*tri*-(4-bromophenyl)-*s*-triazine and 2.375 g (18.3 mmol) $NiCl_2$ were suspended in 100 mL 1,3-diisopropylbenzene in nitrogen atmosphere and heated to 180 °C. 24.6 mL (23.9 g, 144 mmol) triethylphosphite were slowly added. The mixture was heated at 180°C for 20 h. The solvent was removed under reduced pressure. 80 mL each of deionised water and chloroform were added. Aqueous and organic phase were separated and the aqueous phase was extracted with chloroform (4 times 80 mL). The organic phase was dried with $Mg(SO_4)$, which was filtered off and the solvent was removed under reduced pressure.

10.08 g (14.0 mmol, yield 89 %) of colourless solid were recovered.

Elementary analysis: calculated for $C_{33}H_{42}O_9N_3P_3$: C = 55.2 %, H = 5.9 %, N = 5.9 %, found: C = 54.8 %, H = 5.9 %, N = 5.9 %.

^{1}H-NMR (200 MHz, DMSO-D6, 300 K, TMS): δ = 8.87 (dd, 6 H, ^3J = 8.5 Hz, ^4J = 3.8 Hz, H-3), 8.02 (dd, 6 H, ^3J = 12.7 Hz, 8.5 Hz , H-2), 4.11 (m, 12 H, C*H*$_2$), 1.29 (t, 18 H, ^3J = 7.0 Hz C*H*$_3$) ppm.

^{13}P-NMR (200 MHz, DMSO-D6, 300 K, H_3PO_4): 16.60 ppm.

IR ṽ (cm^{-1}) = 2981 (w, C-H str.), 2936 (w, C-H str), 2905 (w, C-H), 1575 (m, C=C str.), 1511 (vs, triazine ring str.), 1478 (w, OCH_2 def.), 1442 (w, CH_3 def.), 1399 (w, C=C str.), 1392 (w, OCH_2), 1369 (m, CH_3 def.), 1357(m, triazine ring str.), 1300 (w, C-H), 1280 (w, C-H def.), 1247 (s,b, P=O str.), 1179 (vw, CH_3 rocking), 1162 (m, rocking), 1153 (m, P-C str.), 1123 (m, P=O), 1097 (m, CH_3 rocking), 1046 (s,b, P-O), 1011 (vs, b, P-O-C_2H_5), 959 (s,b, P-O-C_2H_5), 943 (s,b, P-O-C_2H_5), 867 (w, C-H def.), 850 (w, triazine bend.), 808 (m, C-H def.), 788 (s, P-O-C str.), 756 (s, CPO_3 def.), 702 (s, C-H def.), 634 (w, arom. ring def.), 576 (s, P-C), 534 (s, P-C), 468 (s,b, arom. ring def.).

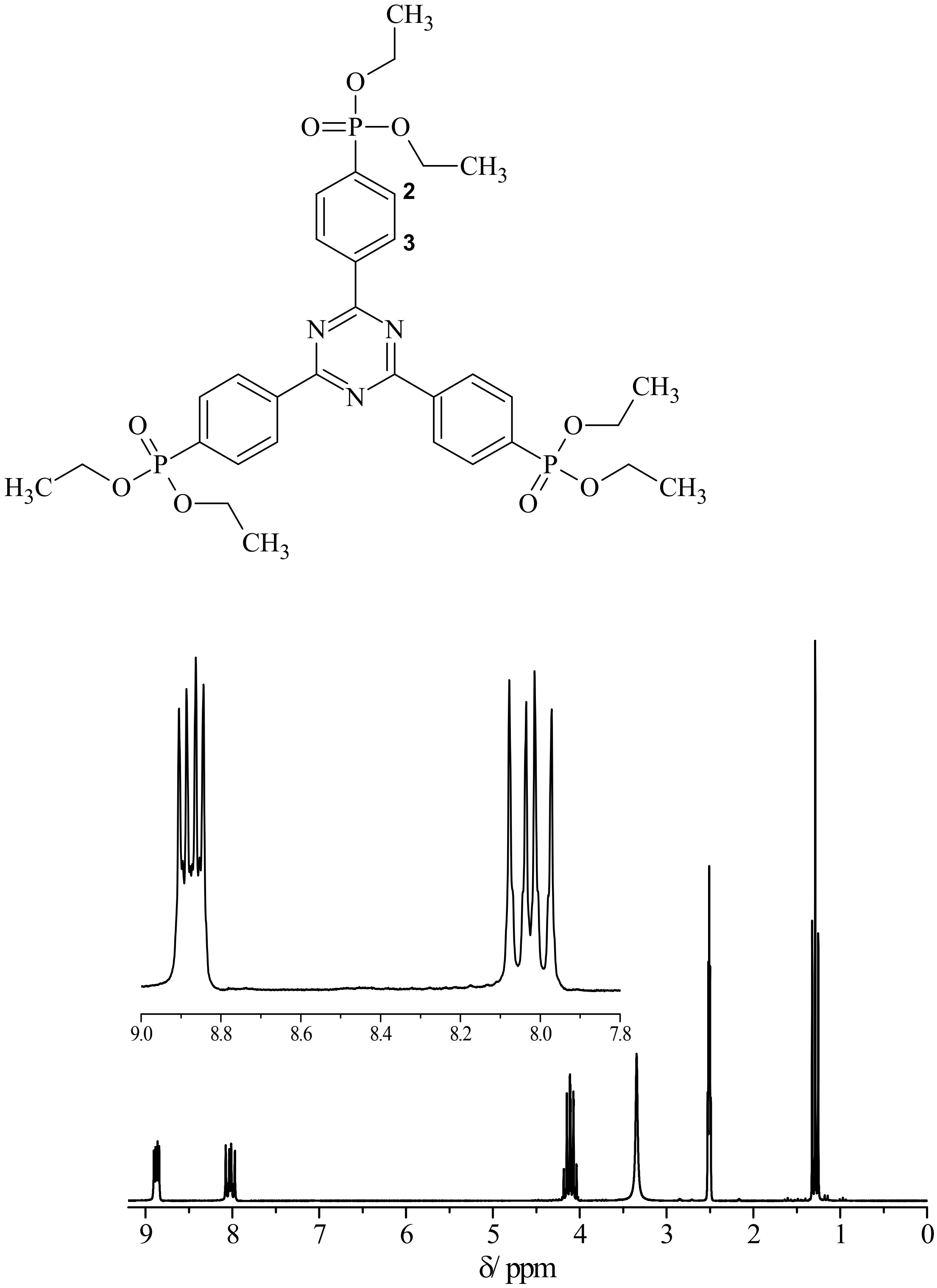

Fig S8 ^{1}H NMR spectrum of 2,4,6-*tri*-(4-diethylphosphonophenyl)-*s*-triazine.

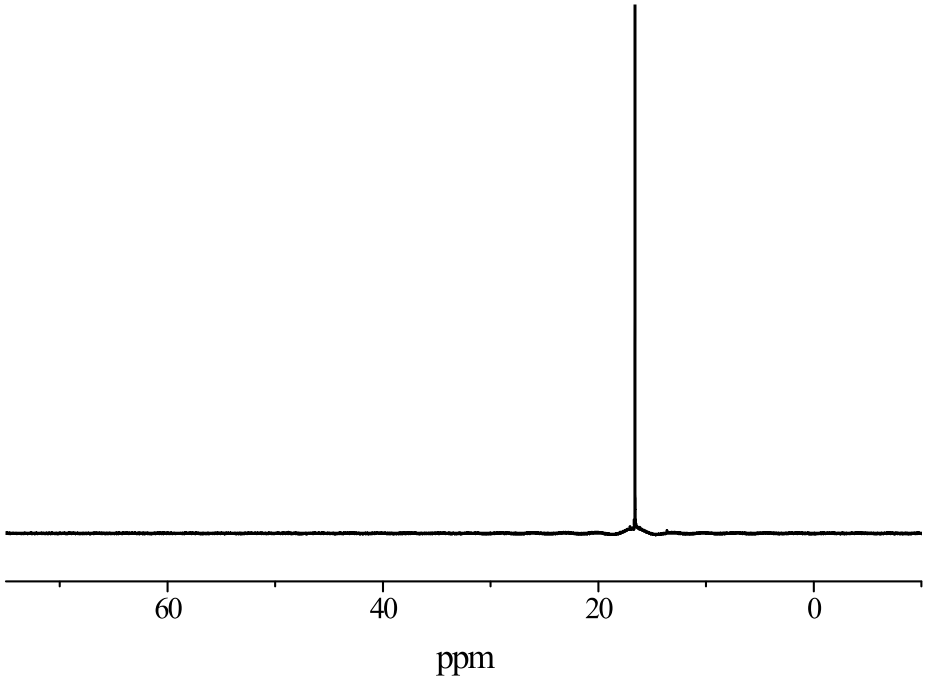

Fig S9 ^{31}P NMR spectrum of 2,4,6-*tri*-(4-diethylphosphonophenyl)-*s*-triazine.

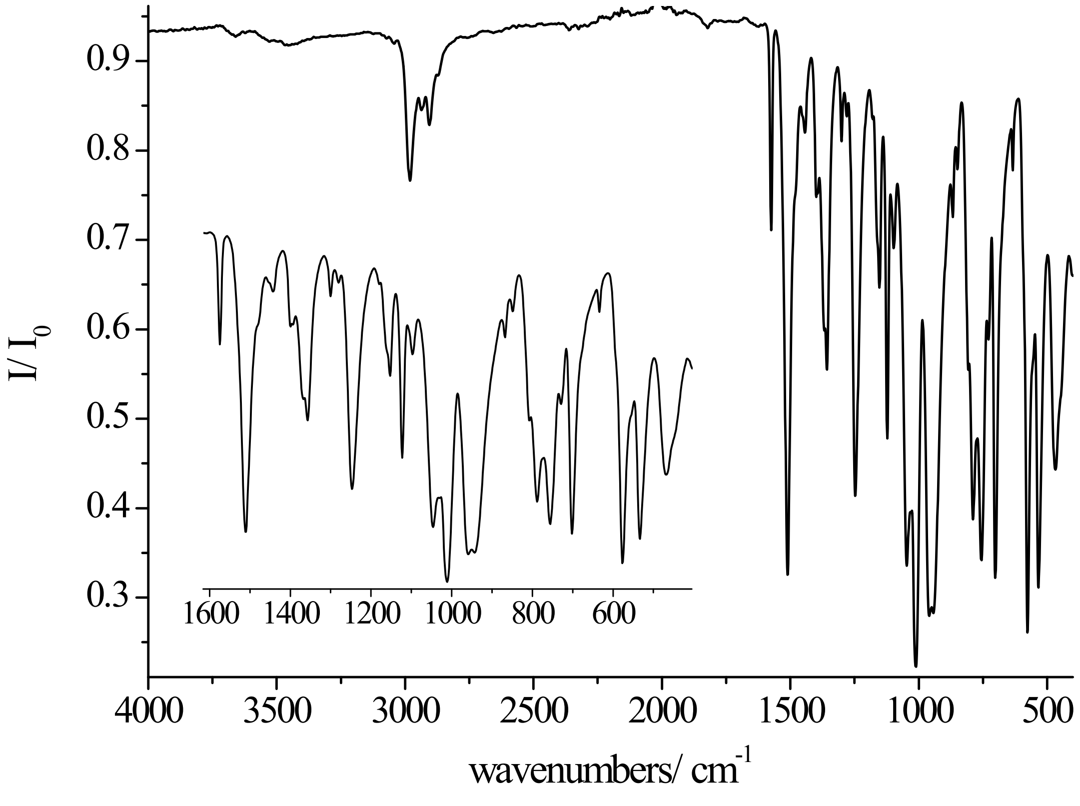

Fig S10 IR spectrum of 2,4,6-*tri*-(4-diethylphosphonophenyl)-*s*-triazine.

Synthesis of 2,4,6-*tri*-(phenylene-4-phosphonic acid)-*s*-triazine

8.75 g (12.2 mmol) of 2,4,6-*tri*-(4-diethylphosphonophenyl)-*s*-triazin were dissolved in 170 mL dichlormethane. Under nitrogen atmosphere 16.7 mL (19.2 g, 125.8 mmol) trimethylsiliylbromide were added. The mixture was stirred for 18 h, afterwards 200 mL of methanol were added. The solvent was evaporated and 100 mL of methanol were added and afterwards evaporated. This was repeated three times.

6.55 g (11.9 mmol, yield 98%) of a yellow solid were recovered.

Elementary analysis: calculated for $C_{33}H_{42}O_9N_3P_3$: C = 45.1 %, H = 3.3 %, N = 7.6 %, found: C = 44.3 %, H = 3.5 %, N = 7.3 %.

^{1}H-NMR (200 MHz, DMSO-D6, 300 K, TMS): δ = 8.74 (dd, 6 H, ^{3}J = 8.4 Hz, ^{4}J = 3.3 Hz, H-3), 7.92 (dd, 6 H, ^{3}J = 12.6 Hz, 8.4 Hz , H-2) ppm.

^{13}P-NMR (200 MHz, DMSO-D6, 300 K, H_3PO_4): 11.49 ppm.

IR $\tilde{\nu}$ (cm^{-1}) = 1575 (w, C=C str.), 1508 (s,b, triazine ring str.), 1401 (w, C=C str.), 1371 (m, C=C str.), 1354 (m,b, triazine ring str.), 1302 (w, C-H), 1154 (m, P-C str.), 1126 (m,b, P=O str.), 1103 (m), 984 (m,b, P-O str.), 918 (s, b, P-O str.), 866 (m, C-H def.), 842 (m, triazine bend.), 803 (s, C-H def.), 782 (m, P-O str.), 744 (m, CPO_3 def), 726 (w), 704 (s, C-H def.), 676 (m), 652 (m), 634 (m, arom. ring def.), 603 (w), 558 (m), 527 (m, b, P-C), 451 (m, P-OH), 435 (m, P-OH).

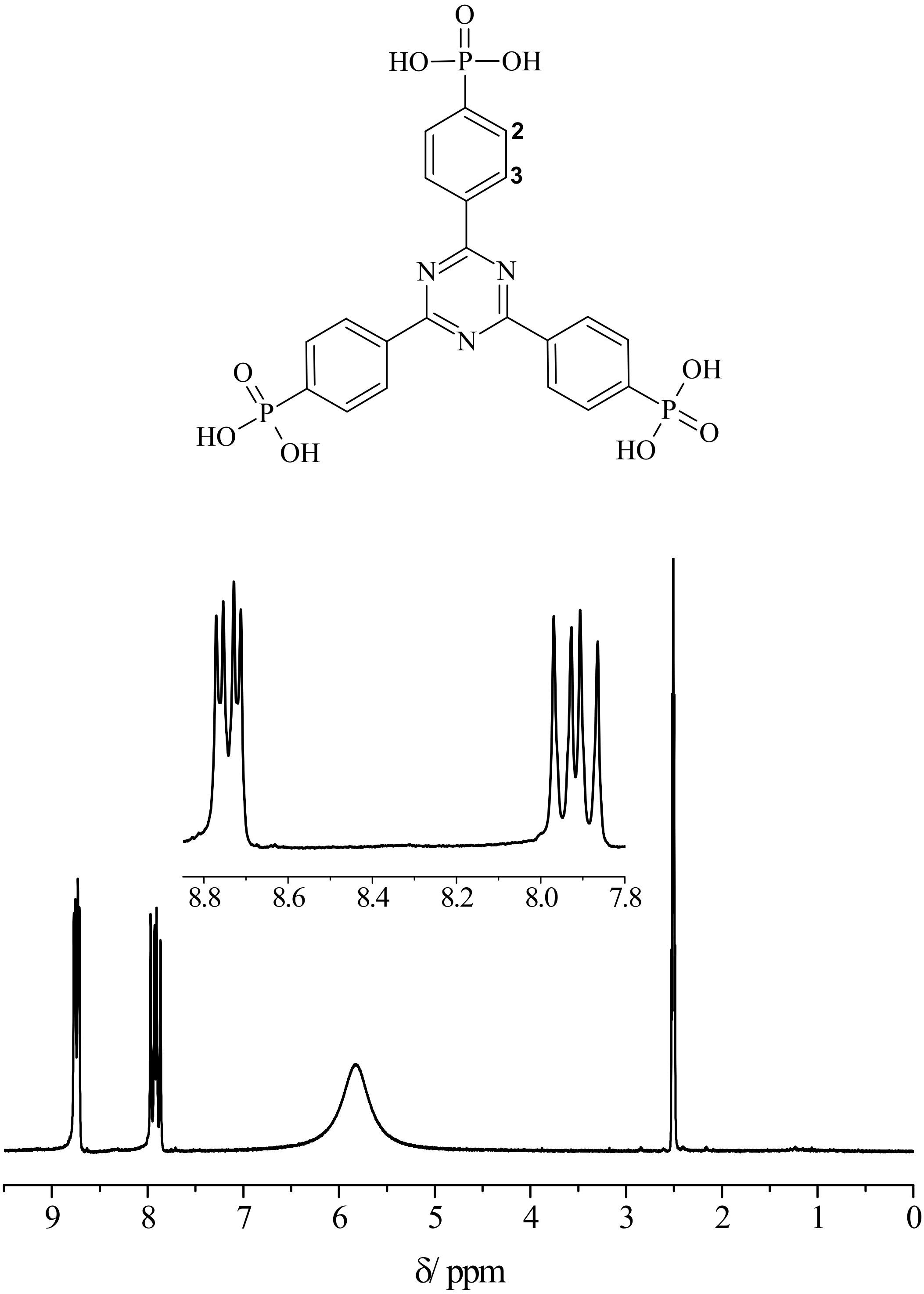

Fig S11 ^{1}H NMR spectrum of 2,4,6-*tri*-(phenylene-4-phosphonic acid)-*s*-triazine.

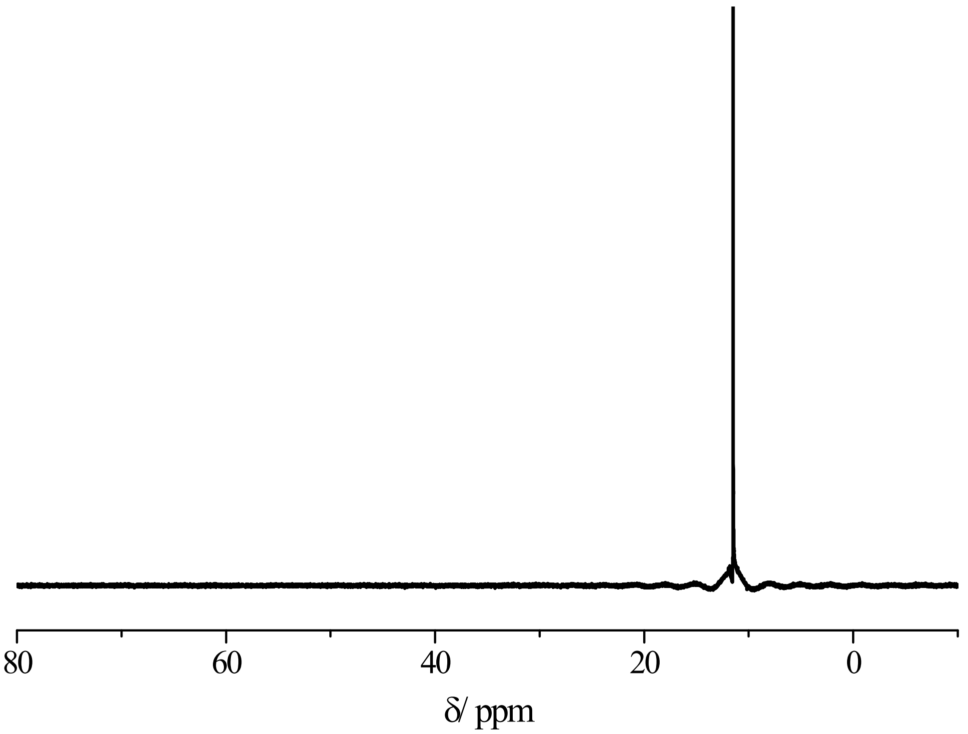

Fig S12 31P NMR spectrum of 2,4,6-*tri*-(phenylene-4-phosphonic acid)-*s*-triazine.

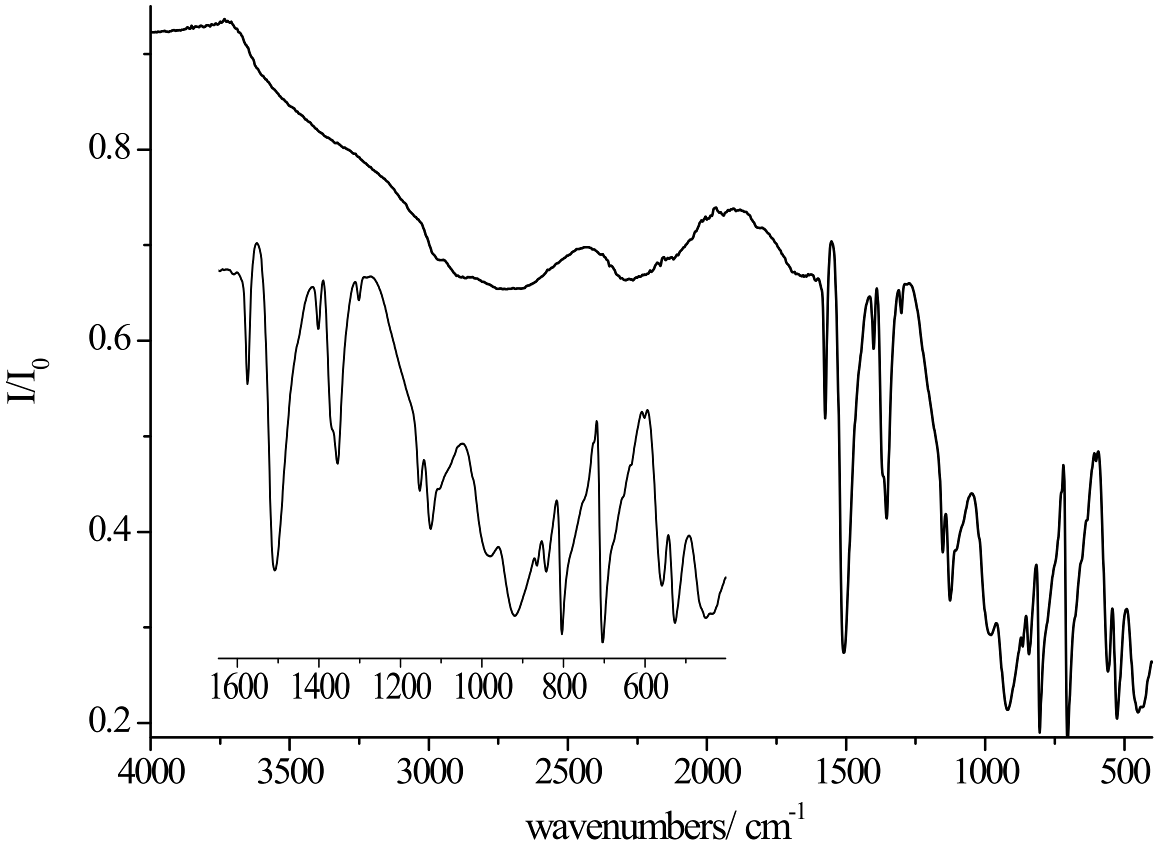

Fig S13 IR spectrum of 2,4,6-*tri*-(phenylene-4-phosphonic acid)-*s*-triazine.

Synthesis of $[Cu_3(PPT)(H_2O)_3]\cdot10H_2O$

70 mg (0.127 mmol) of 2,4,6-*tri*-(phenylene-4-phosphonic acid)-*s*-triazine were introduced in a 2 mL Teflon vial. 713 µL of deionised water, 63.7 µL (0.127 mmol) of a 2 M solution of $Cu(NO_3)_2$ and 223 µL (0.446 mmol) of a 2 M solution of NaOH were added. The vial was sealed and the reactor was heated up to 190 °C for 16 h, heated for 24 h and cooled down for 24 h to room temperature. The precipate was filtered off and washed with water and ethanol.
46 mg of a pale green solid were recovered. (Yield 48% based on H_6PPT)
Elementary analysis: calculated for $Cu_3C_{21}H_{18}O_{12}N_3P_3$: C = 32.0 %, H = 2.3 %, N = 5.3 %, found: C = 32.0 %, H = 3.2 %, N = 5.2 %.

IR ṽ (cm^{-1}) = 1635 (m,b, H2O), 1579 (m, C=C str.), 1513 (s, triazine ring str.), 1410 (w, C=C str.), 1371 (m, C=C str.), 1360 (m, triazine ring str.), 1301 (w, C-H), 1166 (w, C-H def.), 1157 (m, P-C str.), 1131 (s, P=O str.), 1106 (m), 1050 (s,b, P-O), 1017 (m), 991 (s,b, P-O str.), 935 (m,b, P-O str.), 870 (w, C-H def.), 845 (w, triazine bend.), 808 (m, C-H def.), 756 (w, CPO_3 def), 728 (w), 706 (s, C-H def.), 584 (s, P-C), 535 (m, P-C), 491 (m), 473 (m, arom. ring def.).

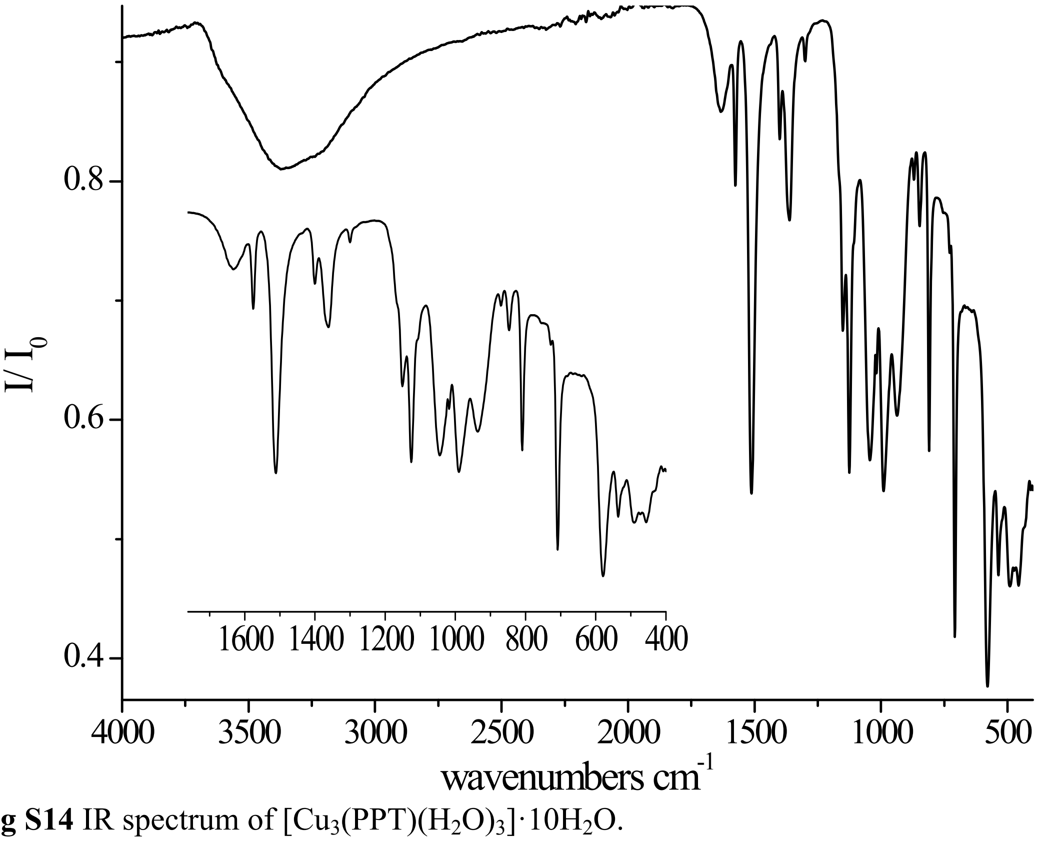

Fig S14 IR spectrum of $[Cu_3(PPT)(H_2O)_3]\cdot10H_2O$.

Analytical methods

Elemental analysis. Carbon, hydrogen and nitrogen contents were determined by elemental analysis by a EuroEA3000, referenced to Sulfanilamide.

Powder X-ray Diffraction. The PXRD patterns were collected in the 0-50 2θ range on a Stoe Stadi P Kombi Diffractometer in transmission geometry, equipped with an Image Plate detector.

Thermogravimetric analysis. Thermogravimetric measurements and differential thermogravimetric analysis was performed under a stream of air (75 mL/min) using a Netsch STA-409CD instrument running from room temperature to 900 °C with a heating rate of 4 K/min.

Nuclear magnetic resonace spectroskopie. ^{1}H-NMR and ^{31}P-NMR spectra were recorded on a Bruker DRX 500 spectrometer. The chemical shift (δ) values are reported in ppm and the coupling constants (J) are given in Hz. The abbreviations are as follows: s singlet, d doublet, dd doublet of a doublet, t triplet, m multiplet.

Scanning Electron Microscopy. SEM images and EDX measurements were performed with a Philips ESEM XL 30 instrument.

Sorption measurements. 20-40 mg $[Cu_3(PPT)(H_2O)_3]\cdot 10H_2O$ were activated under vacuum for 12 hours at 150 °C. N_2, CO_2, H_2 and H_2O sorption measurements were carried out with a Belsorp$_{max}$ (Bel Japan Inc.). The surface area was determined with the BET method,[13] where the range for application of the BET method was determined by a Rouquerol plot.[14] Pore volume was determined at $p/p_0 = 0.5$.

Single Crystal X-Ray Diffraction. Single crystal X-ray diffraction data was collected on a Rigaku Saturn724+ diffractometer at 120 K using a synchrotron radiation (λ = 0.6889 Å) at the beamline I19, Diamond Light Source, Didcot, UK. Data reduction and empirical absorption correction were applied using CrysAlisPro, the data was analysed by XPREP[15] and the structure was solved and refined by SHELX.[16]

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